COED Char Desulfurization Process Studies

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Project COED (Char-Oil-Energy-Development) sponsored by the Office of Coal Research, Department of the Interior, seeks to upgrade the value of coal by conversion to synthetic crude oil, gas, and fuel char. The original scope of Project COED was enlarged to include the production of low-sulfur fuel char to reduce air pollution. Preliminary experimental work (1) showed that the sulfur in COED char can be removed by treatment with hydrogen at 1600° and 1 atmosphere pressure. The rate of desulfurization was severely inhibited by low concentrations of hydrogen sulfide in the reactant gas. It was concluded that a hydrogen sulfide absorbent or acceptor, admixed with char, would be required to make a commercial process viable.

A block diagram of the proposed COED char desulfurization process is shown in Figure 1. Hydrogen and char from the COED pyrolysis plant plus acceptor would be fed to a desulfurization reactor. Here sulfur would be transferred from the char to the acceptor via a hydrogen sulfide intermediate. Desulfurized char and spent or sulfided acceptor would then be separated. Spent acceptor would be regenerated to yield active acceptor for recycle and by-product sulfur. This paper will summarize the results of the experimental program to specify the chemistry and mechanics of each of these steps. A preliminary process flowsheet, and the economics of the process derived from it, will also be presented.

Desulfurization

Desulfurization of COED char in the presence of hydrogen and an acceptor was investigated in a bench-scale rotary kiln. A sketch of this apparatus is shown in Figure 2. The 2-inch diameter kiln was mounted inside a resistance furnace and driven at 6 rpm by an electric motor, speed reducer, and pulley system.

USP calcium oxide and four different calcined dolomites were evaluated as hydrogen sulfide acceptors. Best results were obtained with a calcined dolomite. In 10 minutes, 85 percent sulfur removals were achieved with a hydrogen partial pressure of 15 psi. The sulfur content char from Illinois No. 6-seam coal was reduced from 3 to less than 0.6 weight percent. Only stoichiometric amounts of hydrogen and acceptor were required for the desulfurization reactions:

$$S_{char} + H_2 \rightarrow H_2S \qquad (1)$$

$$CaO \cdot MgO + H_2S \rightarrow CaS \cdot MgO + H_2O \qquad (2)$$
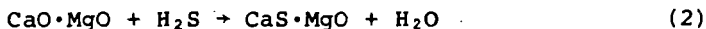
The rate of desulfurization was found to be independent of acceptor particle size in the range of sizes from minus 325-mesh to 6-mesh.
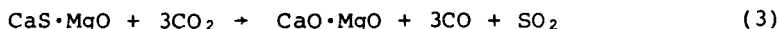
Separation

After desulfurization, spent acceptor must be separated from desulfurized char. The difference in size consist and density between the acceptor and the char suggested that a fluidized bed could be used to separate them. The specific gravity of the acceptor is about 2, compared to about 1 for char. The proposed size consist for the acceptor is 6- x 10-mesh (Tyler) while COED char is all minus 16-mesh.

A 3-inch diameter glass column, equipped with a perforated grid plate and drain legs 1/2 inch and 6 inches above the grid plate, was used to determine the feasibility of separating char and acceptor in a fluidized bed. A sketch of this apparatus is shown in Figure 3. Results of these studies are shown in Figure 4. At a fluidizing velocity of about 2.5 ft./sec., acceptor sank to the bottom of the bed and char was fluidized above it. The acceptor stream, drawn off through the drain leg 1/2 inch above the grid plate, contained about 2 percent char. No acceptor was found in the char product drained from the drain leg 6 inches above the grid plate. Thus, it appears feasible to separate desulfurized char and spent acceptor in a fluidized bed.

Regeneration

Several routes for the regeneration of spent dolomitic acceptor were investigated including carbonation with steam and carbon dioxide (2) and roasting in air or oxygen. The preferred regeneration scheme, however, was found to be the partial oxidation of spent acceptor with CO_2.

$$CaS \cdot MgO + 3CO_2 \rightarrow CaO \cdot MgO + 3CO + SO_2 \qquad (3)$$

A sketch of the apparatus used to explore acceptor regeneration is shown in Figure 5. A Globar-heated furnace was used to obtain temperatures above 2000°F. The reactor consisted of a sealed 3/4-inch I.D. alumina tube. A fixed bed of spent acceptor was formed between two ceramic wool plugs in the center of the bed. Inlet gases were metered through a rotameter. Off-gases were sampled and vented.

The regeneration of spent acceptor with carbon dioxide is catalyzed by iron (3). Acceptor particles were impregnated from solutions of ferric nitrate in methanol resulting in a seven-fold increase in regeneration rate as shown in Figure 6. This rate acceleration was accomplished by increasing the iron content of the dolomitic acceptor from 0.25 weight percent, the naturally occurring iron content, to 0.5 weight percent. Further increases in iron concentration did not increase rates. A microscopic examination of the impregnated acceptor particles showed that iron was concentrated in spots on the surface.

The effect of temperature on the rate of regeneration of iron-impregnated acceptor is shown in Figure 7. Below 2000°F., the rate is highly dependent on temperature with an apparent activation energy of about 103 kcal. Above 2000°F., the apparent activation energy is approximately an order of magnitude lower and appears to be a function of the space velocity. The behavior is indicative of a change in reaction mechanism at a temperature around 2000°F.

The rate of regeneration is zero order with respect to the CaS·MgO concentration of the acceptor. This is shown in Figure 9. Therefore, the rate-controlling step is not the rate of the reaction between solid CaS·MgO and gaseous carbon dioxide.

The rate of regeneration was also found to be independent of gas velocity and acceptor particle size. Therefore, diffusion of carbon dioxide from the gas to the surface of the acceptor particle is not the rate-controlling step.

The addition of carbon monoxide and inerts (nitrogen) to the carbon dioxide feed severely inhibited the regeneration rate. Runs were made at two conditions: 2200°F. and a space velocity of about 12, and 2000°F. and a space velocity of about 2. Results are summarized in Table I. At 2200°F., 10 percent carbon monoxide in the feed gas decreased the rate about 5 times, while 77.4 percent nitrogen decreased the rate about 3 times. At 2000°F., both 10 percent carbon dioxide and 77.4 percent nitrogen decreased the rate about 3.5 times. Thus, a regeneration process must be designed to keep both CO and inert concentrations in the carbon-dioxide reactant gas low.

The effect of space velocity on regeneration rate is shown in Figure 9. At space velocities below 3, the observed relationship between the space velocity and rate appears to be non-linear; at space velocities above 3, a linear relationship appears to hold. The fixed-bed reactor used in these experimental studies can be approximated by a plug-flow reactor at low space velocities and the differential reactor at high space velocities. This probably accounts for the change in shape of the curve (4). On the basis of these results it was concluded that the rate-controlling mechanism is either equilibrium or some surface phenomenon. The kinetic data were too scattered to distinguish between these types of mechanisms.

At a space velocity of 2, about 2 hours are required to achieve 60 percent regeneration.

The deactivation of dolomitic acceptor after repeated cycles of sulfurization and regeneration was studied by exposing the acceptor to alternate atmospheres of hydrogen sulfide and carbon dioxide. The deactivation was studied under two conditions: 1) sulfurization at 1600°F.--regeneration at 2100°F. and 2) sulfurization at 1600°F.--regeneration at 2200°F. The results are displayed as graphs of activity versus cycle number in Figure 10. Activity is defined as the moles of hydrogen sulfide absorbed per 100 atoms of calcium in the acceptor.

At a regeneration temperature of 2200°F., the dolomite was rapidly deactivated. After five cycles the activity was reduced to about 10. At a regeneration temperature of 2100°F., however, the dolomite maintained an average activity of 59 through 10 cycles. There was no clear trend toward loss of activity with increased cycling. It was concluded that dolomitic acceptor would remain about 60 percent active through at least 10 cycles if regeneration temperatures below 2100°F. were employed.
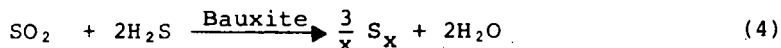
Commercial Process

Based on these bench-scale results, a preliminary flowsheet for a commercial plant was made. The flowsheet is shown in Figure 11, and consists of four major sections: desulfurization in the presence of acceptor, separation of the desulfurized char from the spent acceptor, regeneration of the spent acceptor, and sulfur recovery.

In the desulfurization step, hot char at 1600°F. and hydrogen from the pyrolysis section of the COED plant, react with regenerated acceptor in a rotary kiln. The rotary kiln was chosen because of its ability to mix two dissimilar solids, char and dolomitic acceptor, and to operate with a relatively low gas flow and low pressure drop. Off-gases from the desulfurization reactor are returned to the gas purification section of the COED plant. The solid mixture of desulfurized char and spent acceptor is transported by gravity to the separator.

A fluidized bed was selected as the separation vessel. At a fluidizing velocity of about 2.5 ft./sec., the 6- x 10-mesh sulfided acceptor (specific gravity about 2) sinks to the bottom of the bed while the minus 16-mesh desulfurized char (specific gravity about 1) is fluidized above it. Essentially acceptor-free char is withdrawn from an overflow line at the top of the bed, cooled and sold as a low-sulfur boiler fuel. Sulfided acceptor, containing about 1 percent char, is withdrawn from the bottom of the bed and transported by a bucket elevator to the regeneration reactor. The separation vessel is fluidized by a recycle CO_2 stream. Off-gas from the separator, containing entrained char, is heated to 2600°F. in a wet wall furnace and serves as the fluidizing stream to the regeneration reactor.

The regeneration of spent acceptor is accomplished in a fluidized-bed reactor at 2000°F. Make-up dolomite is also added to the regenerator. Both regeneration and calcination occur in this reactor. Regenerated dolomite is recycled to the desulfurizer. Off-gas from the regenerator, containing CO_2, CO and SO_2, goes to the sulfur recovery section.

In the sulfur recovery section, SO_2-containing off-gases from the regenerator are contacted with hydrogen-sulfide containing gases from the gas purification section of the COED plant. Elemental sulfur is recovered by the standard Claus process:

$$SO_2 + 2H_2S \xrightarrow{\text{Bauxite}} \frac{3}{x} S_x + 2H_2O \qquad (4)$$

Economics

Both capital and annual operating cost estimates for the COED char desulfurization process have been prepared. The estimates are based on adding a desulfurization section to a commercial COED plant processing 3.5 MM tons per year of Illinois No. 6-seam coal (1). 1.82 MM tons per year of 3-percent-sulfur char are processed yielding 1.75 MM tons of 0.6-percent-sulfur char and 91,300 long tons of sulfur.

Capital and annual operating costs are shown in Table II. Capital costs, including indirects, were estimated (5) at $7.17 MM. Annual operating costs, including 13 percent capital charges, were estimated at $2.6 MM. The annual return on investment, plant-level and before taxes, is highly dependent on the price of by-product sulfur. Assuming desulfurized char can be marketed at 100 percent of the value of coal on a Btu basis, the effect of sulfur price on return is shown in Figure 12. At the present price of sulfur (6), $40 per long ton, the annual return on investment, plant-level and before taxes, is 23 percent. At a sulfur price of $30 per long ton, however, the return is only about 10 percent. These estimates compare very favorably with both residual oil desulfurization (7) and stack gas clean-up schemes (8).

Acknowledgment

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TABLE I

Effect of Carbon Monoxide and Inerts on Regeneration Rate

Run No.	Feed Gas Composition, %	Temperature, °F.	Space Velocity, lb. CO_2/hr./lb. acceptor	Average Rate, lb. S/hr./lb. acceptor
R-161	100 CO_2	2200	11.8	0.19
R-162	90 CO_2 10 CO	2200	12.3	0.036
R-166	22.6 CO_2 77.4 N_2	2200	8.8	0.062
R-182	100 CO_2	2000	1.80	0.090
R-199	22.6 CO_2 77.4 N_2	2000	2.0	0.026
R-197	90 CO_2 10 CO	2000	2.9	0.024

TABLE IIA

Cost Summary –
COED Char Desulfurization Process

Fixed Capital Costs ($1,000)

Desulfurizer	$1,820
Separator and Cyclones	604
Bucket Elevator	26
Spent Acceptor Disposal	103
Acceptor Make-up System	163
Recycle Gas Heaters & Blower	1,221
Regenerator and Cyclones	498
Sulfur Recovery System	2,665
Sulfur Storage	27
Acceptor Surge Tank	43
TOTAL*	$7,170

*Includes all indirects and fee.

TABLE IIB

Operating Costs, $/yr.

Capital Related, %			
Taxes & Insurance	2		
Maintenance	6		
Depreciation (20-yr.)	5		
	13		$932,000

Labor-Related	
3 men per shift @ $60M/man-yr.	$180,000

Utilities	
Electricity @ 6 mill/kwh	$ 25,000
Cooling Water @ 2.5¢/M gal.	25,000
Boiler Feed Water @ 40¢/M gal.	50,000
	$100,000

Raw Materials	
Hydrogen @ 25¢/M scf	$409,000
Oxygen @ $6.00/ton	503,000
Dolomite @ $10.00/ton	400,000
Char @ $3/ton	23,000
Iron @ $500/ton	53,000
	$1,388,000

Total Plant-Level Cost, Exclusive of By-product Credit	$2,600,000

FIGURE I

COED CHAR DESULFURIZATION PROCESS
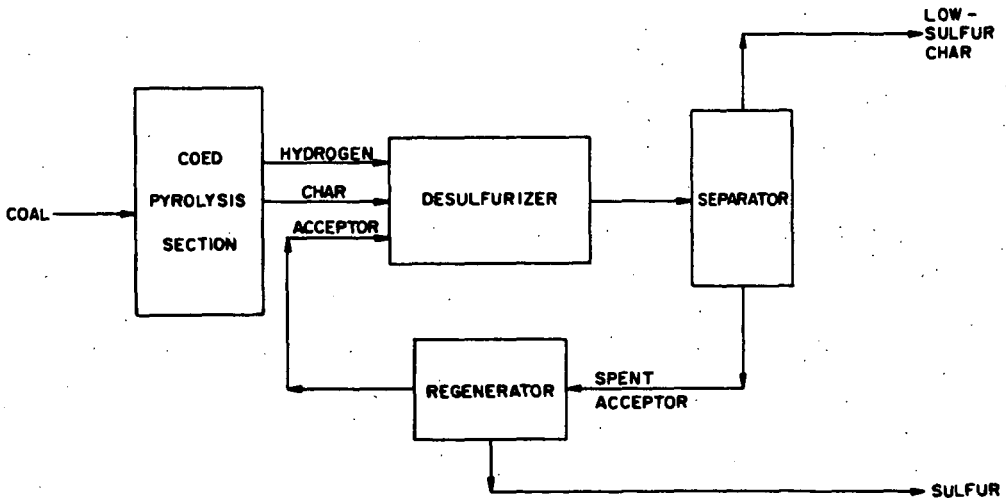
FIGURE 2

TWO-INCH ROTARY KILN FOR CHAR DESULFURIZATION

Ⓐ GAS INLET AND OUTLET

Ⓑ 300 LB. SS FLANGES

Ⓒ RESISTANCE FURNACE

Ⓓ REACTOR-2"-SCH 40-316 SS PIPE

Ⓔ BAFFLES TO KEEP CHAR-ACCEPTOR
   MIXTURE IN REACTION ZONE

Ⓕ FLIGHTS

Ⓖ BEARINGS

Ⓗ 1/8" O.D. SS THERMOWELL

Ⓘ 64:1 SPEED REDUCER

Ⓙ ELECTRIC MOTOR

Ⓟ PRESSURE GAUGE

Ⓣ THERMOCOUPLE
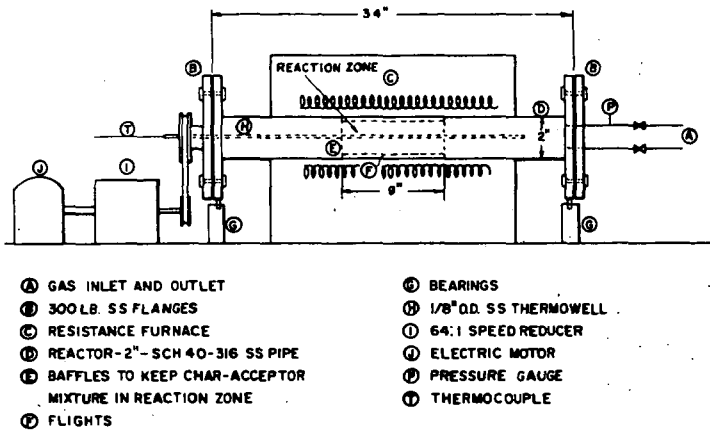
FIGURE 3

FLUIDIZED BED SEPARATOR
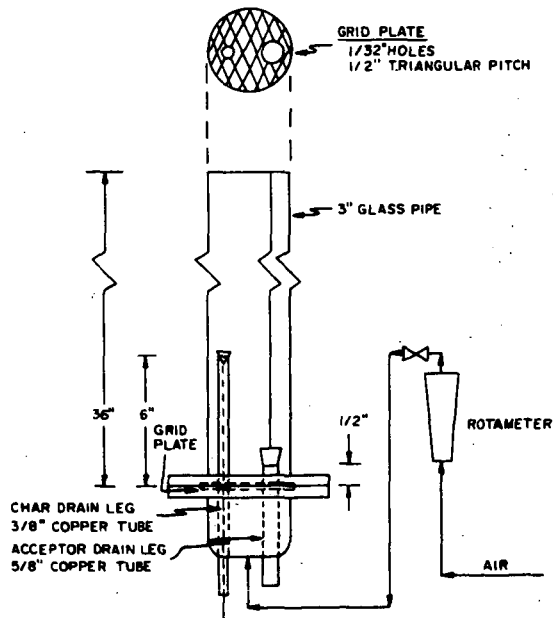
FIGURE 4

SEPARATION OF CHAR AND ACCEPTOR
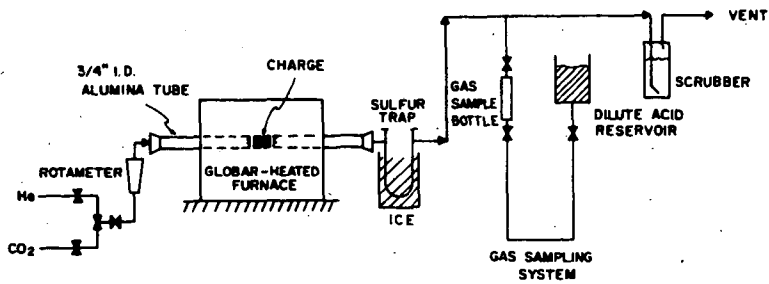IN A FLUIDIZED BED
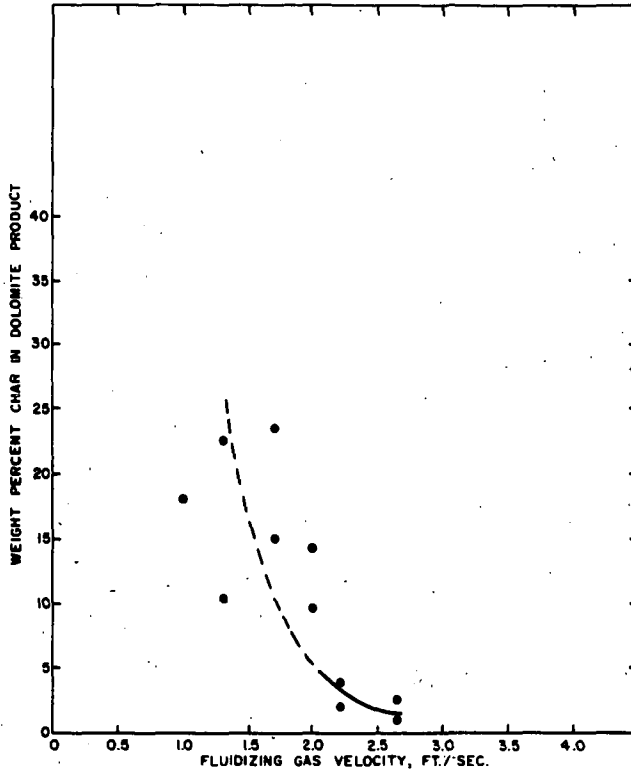
FIGURE 5

APPARATUS USED TO STUDY ACCEPTOR REGENERATION

FIGURE 6

EFFECT OF IRON CONCENTRATION ON
ACCEPTOR REGENERATION
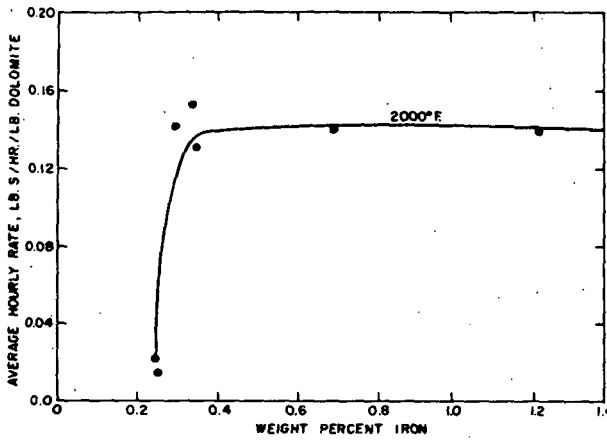
FIGURE 7

EFFECT OF TEMPERATURE ON THE RATE OF REGENERATION
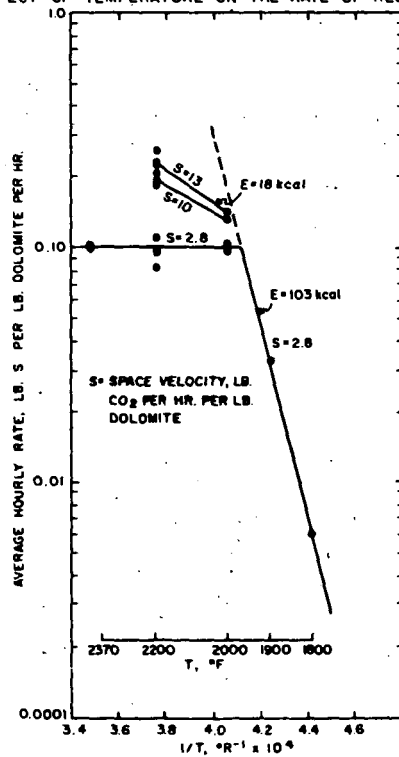
FIGURE 8

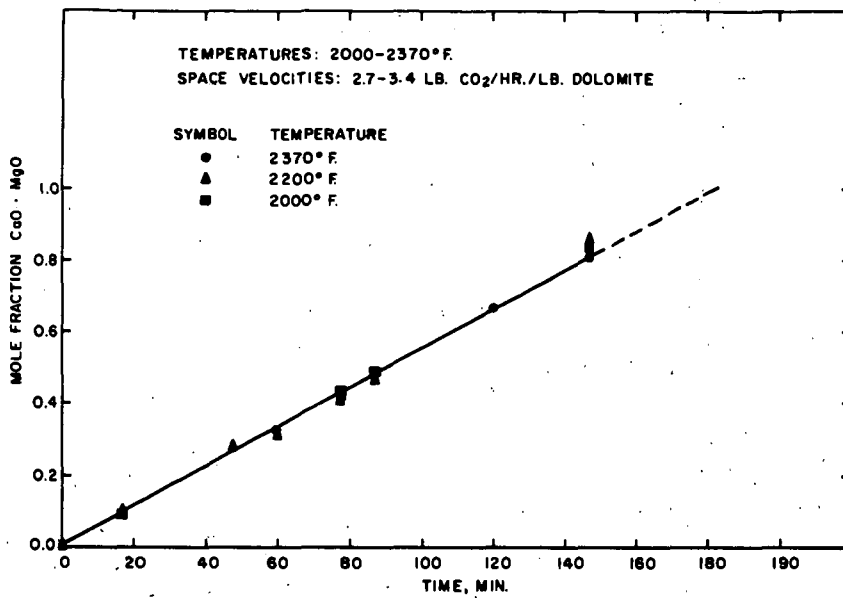MOLE FRACTION CaO·MgO VERSUS TIME
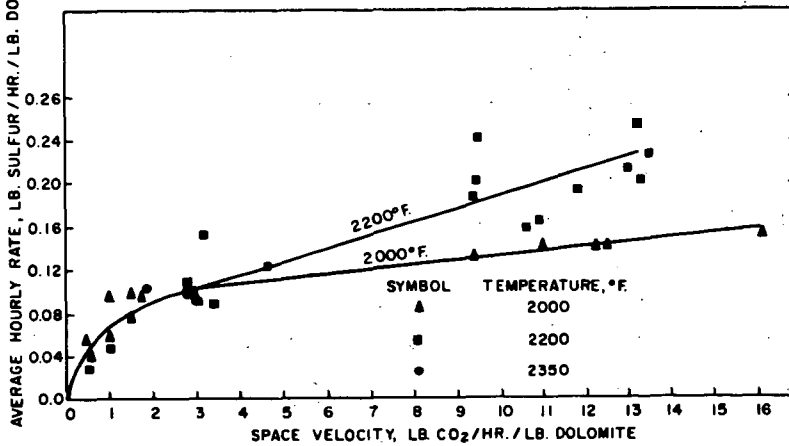

FIGURE 9

EFFECT OF SPACE VELOCITY ON REGENERATION RATE
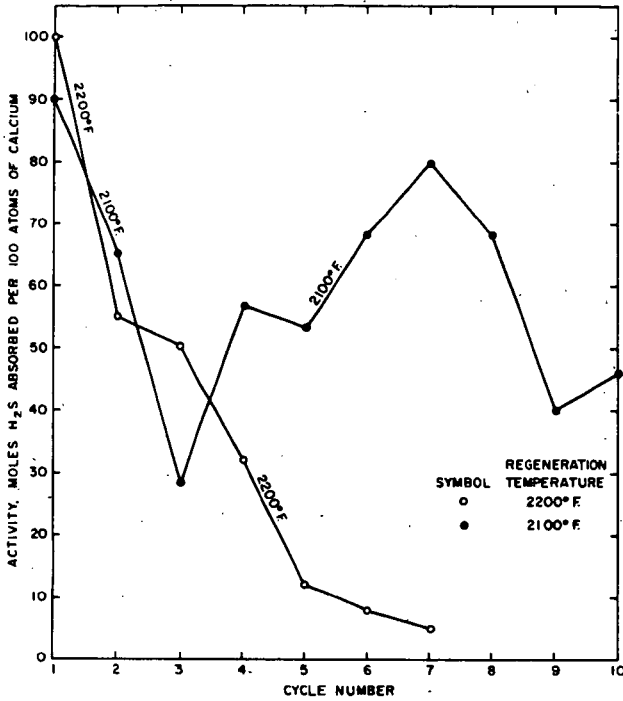
FIGURE 10

DEACTIVATION OF ACCEPTOR UPON CYCLING

FIGURE 12

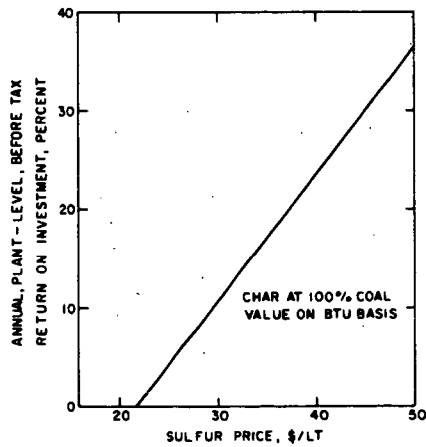EFFECT OF SULFUR CREDIT ON PROCESS ECONOMICS

FIGURE II

COED CHAR DESULFURIZATION PROCESS